THE DENSITY DEPENDENCE OF THE VISCOSITY OF THE NOBLE GASES[1]

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ABSTRACT

As shown by means of computer simulations by Alder et al. and by Michels and Trappeniers the viscosity of hard spheres can be described by the hard-sphere Enskog theory for densities up to double the critical density. Experimental results for simple gases agree with these simulations from the critical density upwards, but for lower densities a sigmoid deviation is found. From the comparison the value of the close-packed molar volume can be determined. The critical molar volume appears to be nearly five times larger than this volume. Therefore, at densities higher than the critical the molecules are within the effective range of the intermolecular potential so that the viscosity can be described by hard-sphere Enskog theory.

For densities lower than the critical the mean distance between the molecules becomes larger than the effective range and we get clusters of molecules. The momentum is then transported by intracluster and intercluster transport. Intracluster transport can be described by a hard-sphere Enskog theory as mentioned above and intercluster transport over the voids by the Chapman-Enskog theory of the mean free path type. The sigmoid curve mentioned above demonstrates the gradual transition from full mean free path transport to full intracluster momentum transport

With this model the viscosity coefficient of the noble gases can be described within the experimental accuracy using three temperature-dependent parameters namely the reduced collision integral Ω^*, the rate of the transition and an integration constant which determines the initial value.

KEY WORDS: density dependence, Enskog theory, intercluster and intracluster momentum transport, noble gases, viscosity.

1. INTRODUCTION

Up to now the only suitable theory which is available to describe viscosity at high densities is the hard-sphere Enskog theory published in 1922[1]. In 1970 Alder et al.[2] proved by means of computer simulations that this theory is valid for hard spheres for densities up to double the critical density. A similar investigation on square-well molecules reported by Michels and Trappeniers[3] confirmed this conclusion by extrapolation of the results. These simulation data are given in terms of the viscosity coefficient relative to the theoretical hard-sphere Enskog value η_{Enskog} as a function of V_0 /V, where V is the molar volume and V_0 the molar volume of close packing.

For comparison with experimental data the latter must also be given relative to η_{Enskog} and expressed in the relative density V_0 /V. V_0 is now an adjustable parameter to bring the real molecules and the hard spheres on the same measure. Such a comparison is shown in Figure 1 for argon. The data are taken from Trappeniers et al.[4], Michels et al.[5], Vermesse and Vidal[6] and Haynes[7] for temperatures from 270 up to 348 K. The value of V_0 has been chosen such that the high density data fit to the solid curve representing the simulation results in the range indicated as IIIB. This criterion results in a constant value for the experimental data in the range indicated as II. This datum is used as a second criterion for the choice of V_0 in cases where high-density data are missing.

The result shown in Figure 1 is also found for other simple gases as methane [8,9] and carbon dioxide[10,11]: in the low density range up to the critical density indicated by the leftmost vertical solid line the results show a sigmoid deviation from hard-sphere Enskog theory, in the intermediate density range II up to nearly twice the critical density the results differ a constant factor from the hard-sphere Enskog value and in the high density ranges IIIA and IIIB up to the melting density the Enskog theory can not be

applied. Recently van der Gulik[12] has shown that in this density range Maxwell's relaxation-time theory given in his second viscosity paper[13] has to be applied.

The deviation with a constant factor found for range II is due to the fact that two different molecule-diameters have to be applied in Enskog theory, as mentioned earlier [14]. According to the hard-sphere Enskog theory the viscosity coefficient η_{Enskog} is given by

$$\eta_{Enskog} = \eta_{0hs}\, E(V), \qquad (1)$$

where η_{0hs} stands for the hard-sphere Chapman-Enskog formula

$$\eta_{0hs} = (5/16)\,(\pi mkT)^{1/2} / \pi\sigma_C^{\,2} \qquad (2)$$

and E(V) for the extension of the theory to higher densities,

$$E(V) = 1/\chi + 0.8\, b / V + 0.7614\, (b / V)^2\, \chi\,. \qquad (3)$$

χ is the radial distribution function at contact, taken from the Carnahan-Starling equation of state for hard spheres and b the Van der Waals co-volume given in terms of V_0. The value of V_0 found in the way mentioned above is slightly temperature dependent due to the fact that the molecules are not really hard: at high temperatures the molecules move faster, collide with greater impact and penetrate each other further than at low temperatures. Also the corresponding diameter decreases with the temperature. However, the collision cross-section $\pi\sigma_C^{\,2}$ is not temperature dependent and therefore, σ_C differs from the diameter corresponding to V_0. σ_C is now chosen such that the Enskog theory gives an accurate description of the experimental results in range II. For less simple molecules like methane and carbon dioxide a form factor has to be added[11]. This second step in the analysis has

been applied in Figure 2 to the measurements of the viscosity of krypton by Trappeniers et al.[15] and by van den Berg[16] and is indicated as SET.

2. THE CRITICAL DENSITY

Why can the viscosity coefficient be described by this special version of the hard-sphere Enskog theory for densities above the critical density but not for densities below the critical density, while the Enskog theory is valid for both density ranges for hard spheres? In all cases considered up to now the critical density appears to be nearly equal to $V_0 /V = 0.21$. Thus, the critical molar volume is nearly equal to five times the molar volume of close packing so that at the critical density the mean distance between the molecules is about 1.7 times the diameter of the molecules. This distance corresponds very nearly to the effective range of the intermolecular forces. At densities higher than the critical the attractive spheres overlap, the attractive forces on the molecules compensate each other, they act only as a background force and the molecules can be handled as soft spheres. Therefore, at these densities the viscosity η_{SET} can be described in terms of the special Enskog theory as mentioned above.

At densities somewhat lower than the critical the mean distance between the molecules becomes larger than the effective range of the intermolecular potential and we get clusters of molecules held together by the intermolecular forces, interspaced with empty cracks. With further decreasing density the clusters become smaller and smaller: trimers and dimers at atmospheric pressure and single gas-molecules at still lower pressure. Thus, at densities lower than the critical a gas is mesoscopically homogeneous, but microscopically, on the level of atoms, inhomogeneous, a mixture of clusters and voids.

3. THE VISCOSITY AT LOW DENSITIES

At very low density only single molecules remain and the viscosity coefficient can be described with the full Chapman-Enskog theory, which is in essence a mean free path theory. At the critical density the viscosity coefficient is given by the special Enskog theory as mentioned above. In between, however, we have to cope with two transport mechanisms: intracluster momentum transport inside the clusters and intercluster momentum transport over the voids in between them. This two mechanisms model is an unavoidable consequence of the existence of clusters.

The gradual transition from the mean free path mechanism at very low density to the hard-sphere Enskog mechanism at the critical density as a function of the density is demonstrated by the sigmoid curves in range I in Figure 2. The temperature dependence reflects the temperature dependence of the reduced collision integral Ω^* in the Chapman-Enskog part. Therefore, the momentum transport between the clusters over the voids is considered to be of the mean free path type as described by the Chapman-Enskog theory. A good choice for the momentum transport within the clusters appears to be given by the special Enskog theory.

According to model theory we have to look for the change in the density dependence of the contribution $F(\rho)$ of the intracluster transport: $\partial F(\rho)/\partial(\rho)$. This contribution is determined by the amount and magnitude of the clusters and these change during collisions. Therefore, $\partial F(\rho)/\partial(\rho)$ is proportional to both the contribution $F(\rho)$ of the intracluster transport and the contribution $1 - F(\rho)$ of intercluster transport:

$$\partial F(\rho/\rho_c) / \partial(\rho/\rho_c) = r\, F(\rho/\rho_c)\, \{1 - F(\rho/\rho_c)\}, \quad (4)$$

where r is the rate of transition and the density ρ is normalised with the critical density ρ_c for convenience. This equation is known as the logistic equation. Its integration results in:

$$F(\rho/\rho_c) = 1 / \{ 1 + \exp (C - r\, \rho/\rho_c)\}. \quad (5)$$

where C is an integration constant depending on the initial conditions.

Applying this model to the present case

$$\eta = F\, \eta_{SET} + (1 - F)\, \eta_0\, E(V) , \quad (6)$$

where $\eta_{SET} = \eta_{0SET}\, E(V)$ and the intercluster transport is of the mean free path type as described by the Chapman-Enskog theory. $\eta_0\, E(V)$ is related to the hard-sphere Enskog value by $\eta_0 = \eta_{0SET} / \Omega^*$, so that

$$\eta = \eta_{0SET}\, E(V)\, [F + (1 - F) / \Omega^*] , \quad (7)$$

$$\eta = \eta_{0SET}\, E(V) / \Omega^* [1 + (\Omega^* - 1) F] \quad (8)$$

and

$$\eta = \eta_{0SET}\, E(V) / \Omega^* [1 + (\Omega^* - 1) / \{1 + \exp(C - r\, \rho/\rho_c)\}] . \quad (9)$$

4. APPLICATION TO THE NOBLE GASES

This model is applied to the neon data of Trappeniers et al.[17] and of Vermesse and Vidal [18], as shown in Figure 3. The agreement is within a few parts per thousand. Figure 4 shows the argon data taken from Michels et al.[5], Vermesse and Vidal[6], Haynes[7] and Gracki, Flynn and Ross[19] for temperatures from 173 up to 348 K. In this large temperature range the agreement is within a percent. Figure 5 shows the fit for krypton where again the data of Trappeniers et al.[15] and of van den Berg[16] are used. Because of the very high accuracy of the data of Van den Berg these data are fitted with a

high weight. Finally, in Figure 6 the result for unpublished data of xenon is shown. These data are taken with the vertical capillary viscometer at the Van der Waals Laboratory. They show that deviations due to the compressibility in the critical region can easily be detected. Also it is seen that the short isotherm at 273.15 K, below the critical temperature, shows the same character. The value of the parameters is rather uncertain in this case due to lack of number and accuracy. For the same reason results for helium could not be given. The figures show that the model is valid up to roughly twice the critical density, at higher densities the deviations increase very fast with the density.

The magnitude of the temperature range for argon makes it possible to approximate the values of V_0, r and C by quadratic functions in $T-T_c$:

$$V_0 = 15.753 - 0.0194918\,(T - T_c) + 4.34407\text{E-}05\,(T - T_c)^2 \qquad (10)$$

$$r = 2.35588 + 0.00616478\,(T - T_c) + 5.84897\text{E-}05\,(T - T_c)^2 \qquad (11)$$

$$C = 1.07297 + .000143397\,(T - T_c) + 2.09386\text{E-}05\,(T - T_c)^2 . \qquad (12)$$

The agreement is hardly influenced by this procedure, showing that the values of r and C are not very critical. Therefore, in general 20 to 30 data are needed to determine these values for one isotherm.

Finally, the value of the parameters is given in Tables I and II. The value of V_{0C} determines the value of the collision cross-section $\pi\sigma_C^2$. As seen, the values of V_0 and Ω^* decrease with the temperature, as expected, and the values of r and C increase with the temperature. Also given are the number of data used to determine these values. The result at 308.15 K for Argon shows that 9 data are not enough to determine an accurate value, the approximation by a quadratic function in $T-T_c$ given above gives nearly the same result. In conclusion it may be said that the result is very satisfying.

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Table I. General Data of Noble Gases

	M	T_c (K)	ρ_c ($kg.m^{-3}$)	V_{0C} ($m^3 \cdot Mmol^{-1}$)
Neon	20.183	44.4	484	6.85
Argon	39.948	150.663	531	15.75
Krypton	83.8	209.4	919	19.75
Xenon	131.3	289.73	1099	26.2

Table II The Temperature Dependent Model Parameters of the Noble Gases

	T(K)	V_0(m^3.$Mmol^{-1}$)	Ω*	r	C	N	
Neon	348.15	5.5868	1.015	7.451	4.595	28	[17]
	323.15	5.6177	1.030	4.027	2.537	29	[17]
	298.15	5.7091	1.056	2.122	1.197	38	30 [17], 8 [18]
Argon	348.15	13.5765	1.142	5.903	1.982	26	[5]
	323.15	13.7195	1.192	4.945	1.563	26	[5]
	308.15	13.7458	1.095	8.509	4.980	9	[6]
	298.15	13.8870	1.215	4.746	1.684	55	25 [5], 20 [7], 10 [19]
	273.15	14.0364	1.301	3.802	1.272	6	[5]
	270.15	13.9142	1.287	3.824	1.283	38	[7]
	223.15	14.6280	1.432	3.258	1.316	34	18 [7], 16 [19]
	173.15	15.3272	1.721	2.483	1.150	61	40 [7], 21 [19]
Krypton	348.15	17.6482	1.312	4.089	1.381	60	24 [15], 36 [16]
	323.15	17.8048	1.358	3.843	1.346	26	[15]
	298.15	18.0482	1.399	3.939	1.592	61	26 [15], 35 [16]
Xenon	348.15	24.1970	1.488	4.315	1.620	25	
	323.15	24.4479	1.480	4.785	2.122	21	
	298.15	24.8187	1.511	5.499	2.488	13	
	273.15	25.3	1.672	4.42	1.885	7	

FIGURE CAPTIONS

Fig. 1. The relative viscosity η / η_{Enskog} of argon as a function of the relative density V_0 /V.

The curve represents the simulation data.

Experimental data: [4] ◆ 323 K, ■ 301 K, [5] x 348 K, O 323 K, + 298 K, ✧ 273 K, [6] ● 308 K, [7] Δ 298 K, ▷ 270 K.

Fig. 2. The relative viscosity η/η_{SET} of krypton as a function of the relative density V_0 /V.

The curve represents the simulation data.

Experimental data: [15] × 348 K, O 323 K, + 298 K, [16] 348 K, ✧ 298 K.

Fig. 3. The viscosity of neon as a function of density and the deviations from the theoretical model in parts per thousand. The curves represent the theoretical model.

Experimental data: [17] × 348 K, O 323 K, + 298 K, [18] ● 298 K.

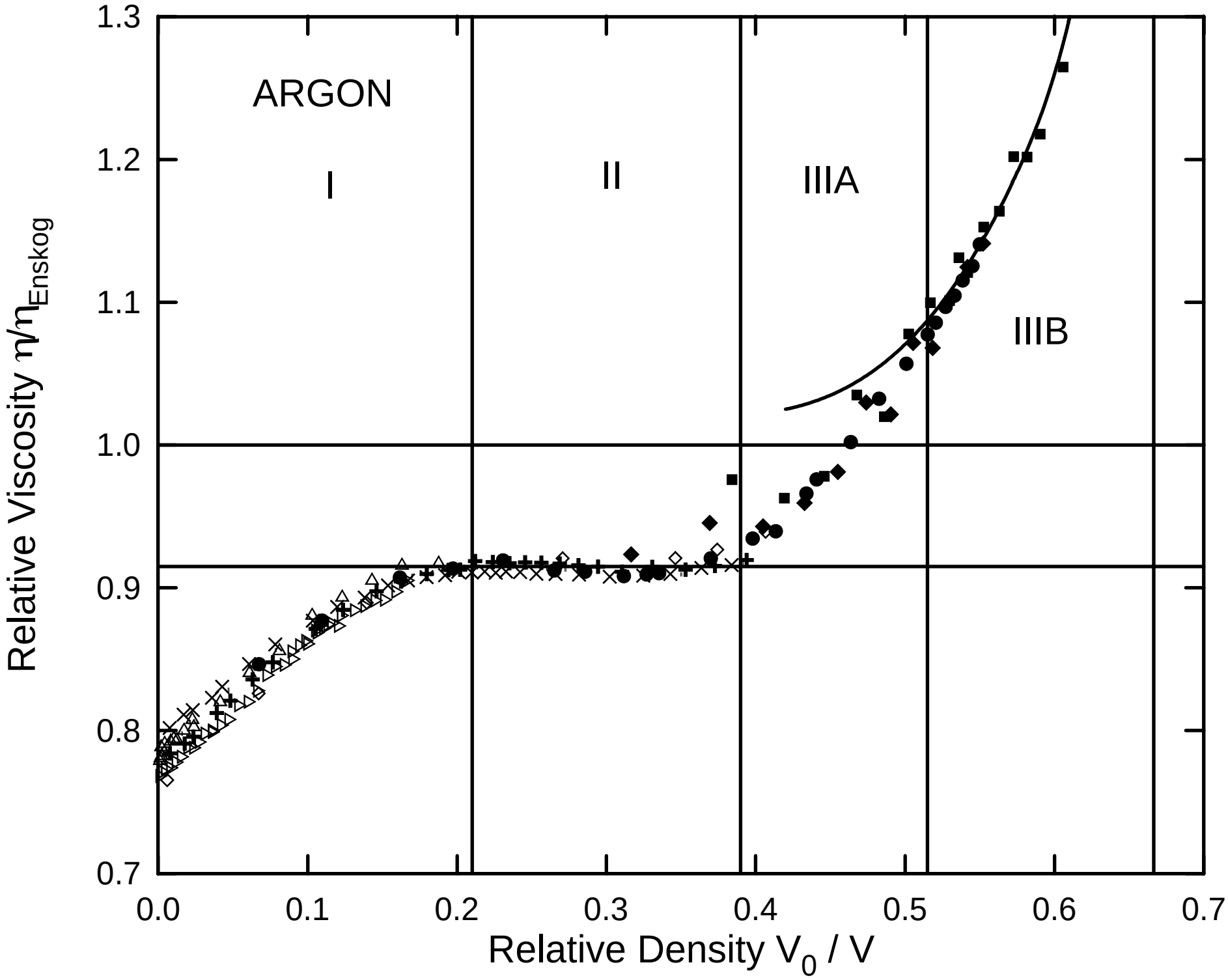
Fig. 4. The viscosity of argon as a function of density and the deviations from the theoretical model in parts per thousand. The curves represent the theoretical model.

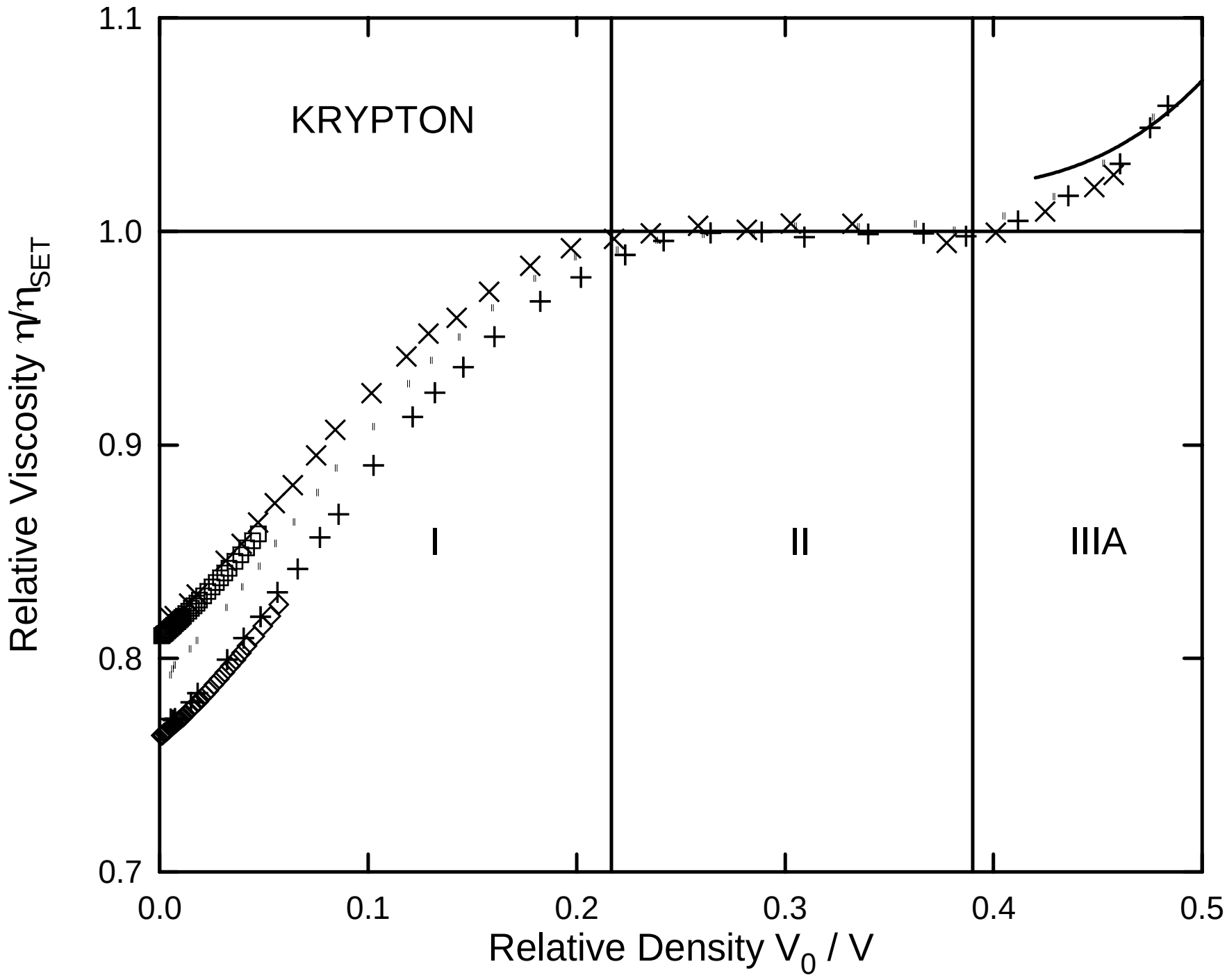
Experimental data: [5] x 348 K, O 323 K, + 298 K, ✧ 273 K, [6] ● 308 K, [7] Δ 298 K, ▷ 270 K, ◁ 223 K, ∇ 173, [19] ◆ 298 K, 223 K, ■ 173 K.

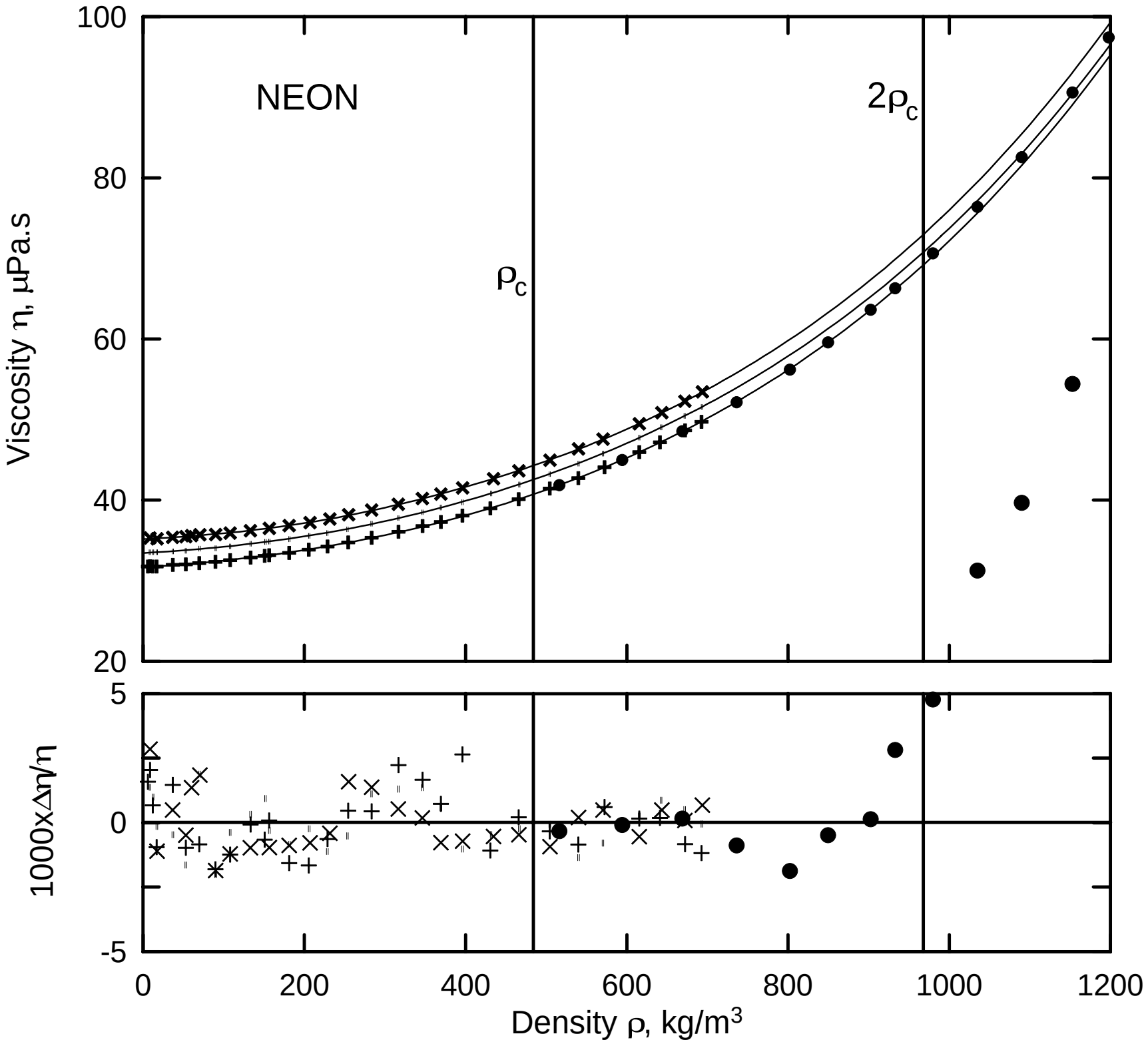
Fig. 5. The viscosity of krypton as a function of density and the deviations from the theoretical model in parts per thousand. The curves represent the theoretical model.

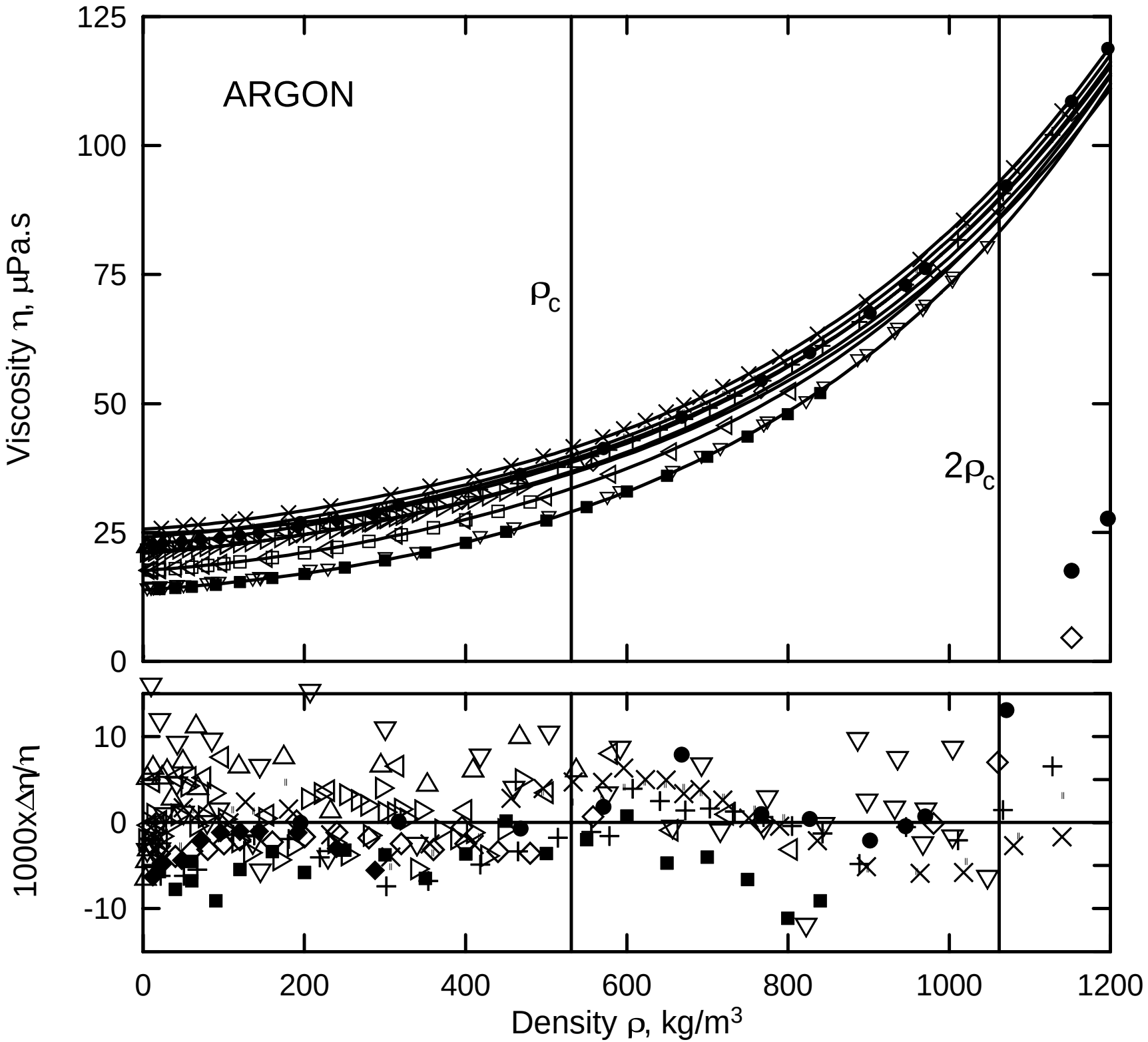
Experimental data: [15] × 348 K, O 323 K, + 298 K, [16] 348 K, ✧ 298 K.

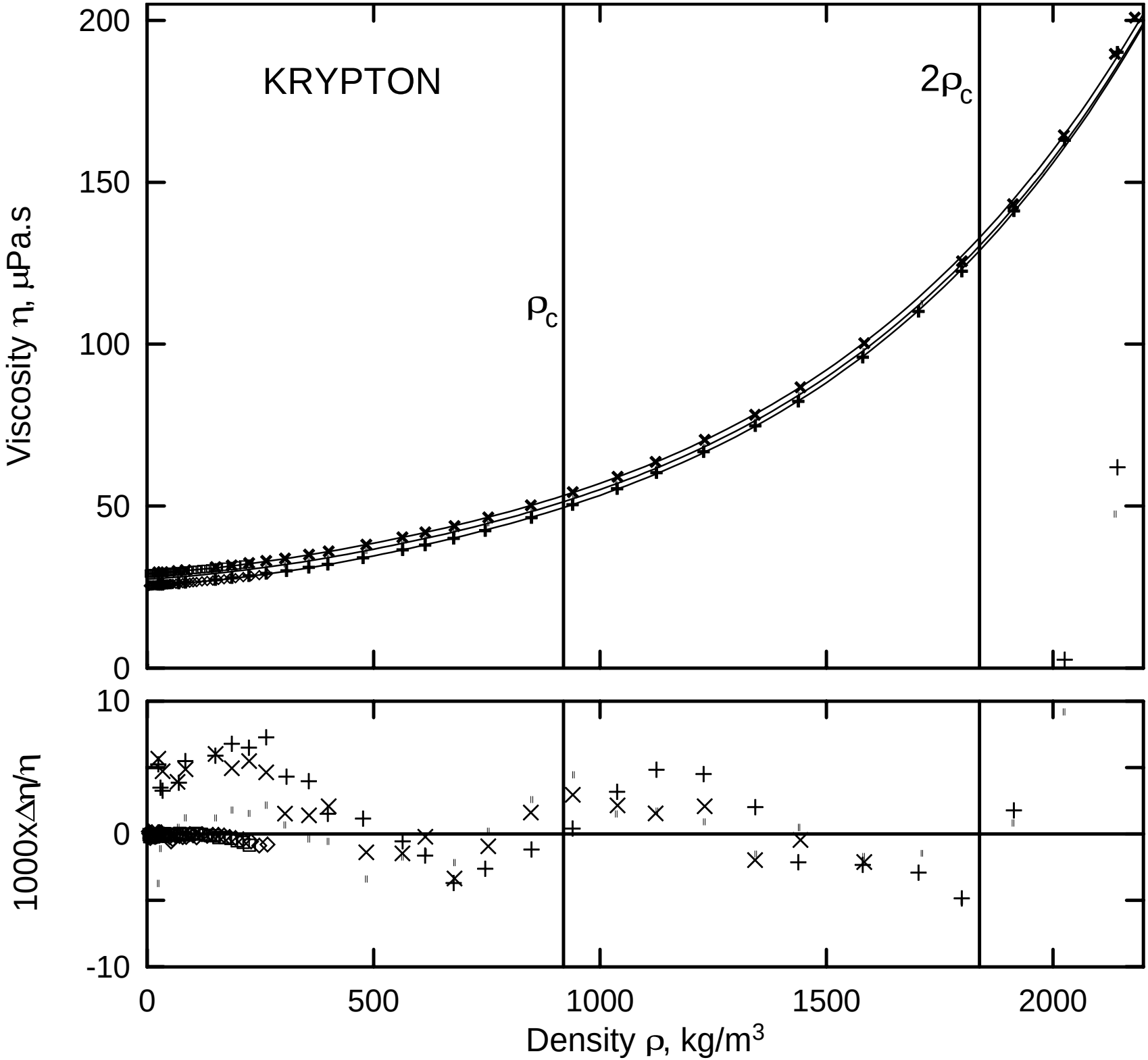
Fig. 6. The viscosity of xenon as a function of density and the deviations from the theoretical model in parts per thousand. The curves represent the theoretical model. Experimental data: × 348 K, O 323 K, + 298 K.

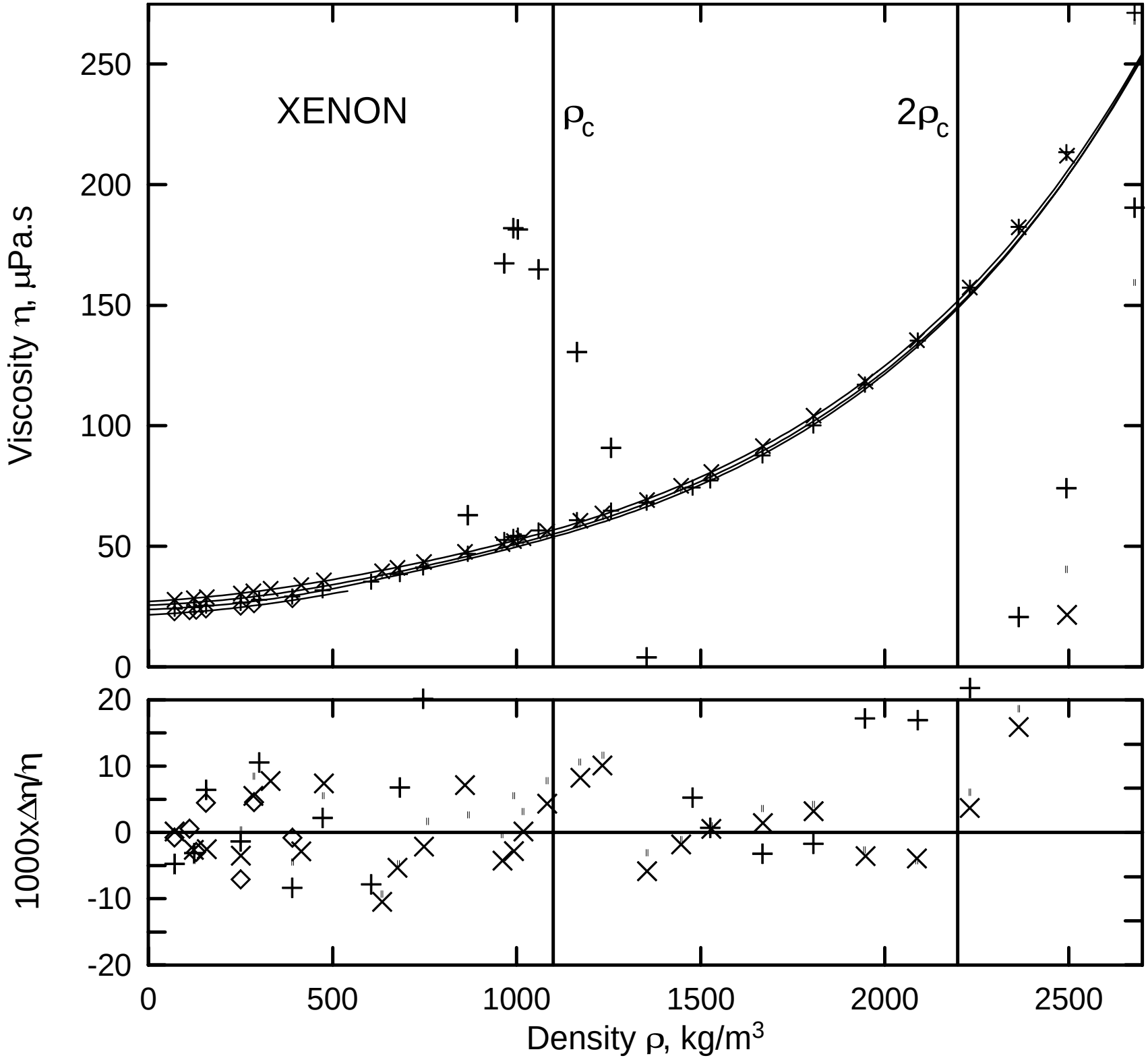

ARGON
I
II
IIIA
IIIB
Relative Viscosity η/η_Enskog
Relative Density V_0 / V
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7


KRYPTON
I
II
IIIA
Relative Viscosity η/η_SET
Relative Density V_0 / V
1.1
1.0
0.9
0.8
0.7
0.0
0.1
0.2
0.3
0.4
0.5


NEON
$2\rho_c$
ρ_c
Viscosity η, μPa.s
100
80
60
40
20
5
0
-5
1000xΔη/η
0
200
400
600
800
1000
1200
Density ρ, kg/m^3


ARGON
Viscosity η, μPa.s
1000xΔη/η
Density ρ, kg/m3
ρc
2ρc
125
100
75
50
25
0
10
0
-10
0
200
400
600
800
1000
1200


KRYPTON
$2\rho_c$
ρ_c
Viscosity η, μPa.s
200
150
100
50
0
1000xΔη/η
10
0
-10
0
500
1000
1500
2000
Density ρ, kg/m^3


XENON
ρ_c
$2\rho_c$
Viscosity η, μPa.s
1000xΔη/η
Density ρ, kg/m^3
250
200
150
100
50
0
20
10
0
-10
-20
0
500
1000
1500
2000
2500